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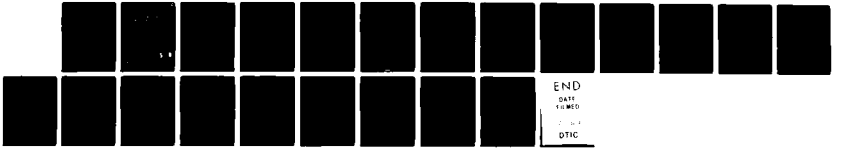

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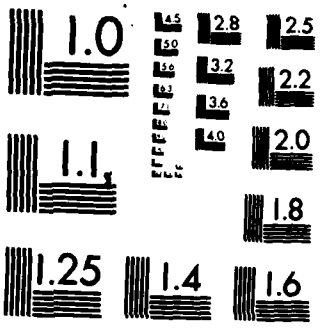

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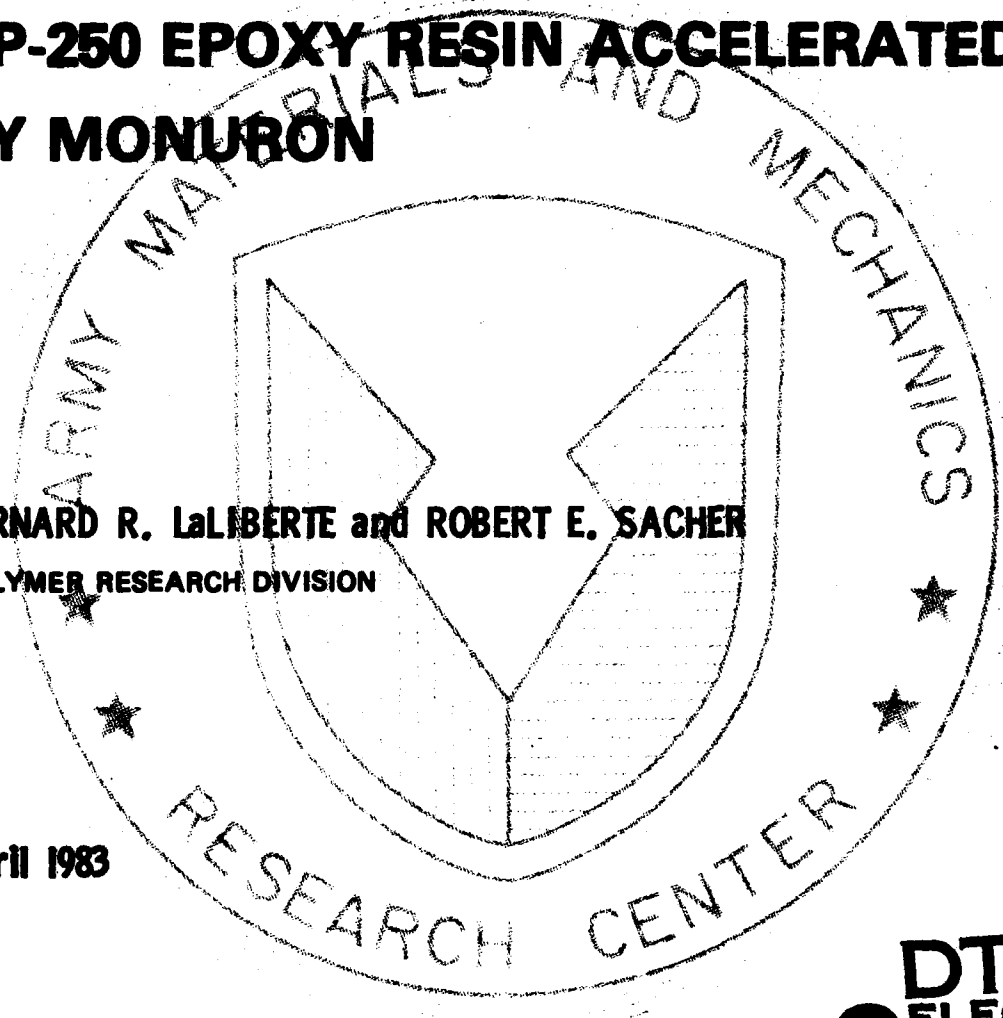
THE DICYANDIAMIDE CURE OF SP-250 EPOXY RESIN ACCELERATED BY MONURON

BERNARD R. LaLIBERTE and ROBERT E. SACHER
POLYMER RESEARCH DIVISION

April 1983



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AMMRC TR 83-17	2. GOVT ACCESSION NO. AD-A129 467	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE DICYANDIAMIDE CURE OF SP-250 EPOXY RESIN ACCELERATE BY MONURON		5. TYPE OF REPORT & PERIOD COVERED Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Bernard R. LaLiberte and Robert E. Sacher		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Army Materials and Mechanics Research Center Watertown, Massachusetts 02172 DRXMR-OP		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS D/A Project: 1L162105AH84 AMCMS Code: 612105.H840011 Agency Accession: DA OD4815
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Materiel Development and Readiness Command, Alexandria, Virginia 22333		12. REPORT DATE April 1983 13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Epoxy resins
Curing agents
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ABSTRACT

The synergistic effect of dicyandiamide and Monuron which takes place in the hardening of epoxy resins was investigated by differential scanning calorimetric analysis conducted under dynamic conditions. The cure behavior was illustrated by the examination of three distinct systems: SP-250 epoxy resin + dicyandiamide (Dicy), resin + Dicy/Monuron, and resin + Monuron. The activation energies of these systems were found to be 39, 22, and 19 kcal/mole, respectively. The by-product of the resin + Monuron reaction is dimethylamine and it was found that this amine is able to enhance the reactivity of dicyandiamide dramatically. Mixtures pertinent to the SP-250 formulation were examined and the interpretation of the thermal data afforded certain speculations.

CONTENTS

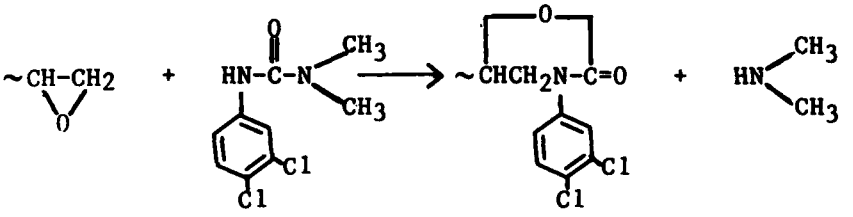
INTRODUCTION

The hardening of dicyandiamide (Dicy)-containing epoxy resins is a high temperature process where an effective cure is realized at approximately 200°C. In contrast, with the addition of trisubstituted urea accelerators such as N-(4-chlorophenyl)-N^1, N^1-dimethylurea (Monuron), these systems can be cured at temperatures even lower than 130°C.

The synergistic effect of dicyandiamide and Monuron in epoxy cures was demonstrated with the SP-250 system manufactured by the 3M Company of St. Paul, Minnesota. The synergy was recorded under dynamic conditions with differential scanning calorimetry (DSC).

DISCUSSION AND RESULTS

Dimethylamine is known to react with epoxy resins and interest in the cure mechanism was heightened when it was observed[1] that a trisubstituted urea/epoxy mixture readily generated the amine. The speculation of a low temperature cyclocondensation reaction occurring between the aryl urea and the oxirane ring was supported by Iwakura and Izawa[2] and this prompted a mass spectrometric (MS) study[3] in this laboratory. The MS analysis of the reaction of a trisubstituted urea with p-tert-butylphenyl glycidyl ether yielded a molecular ion ascribable to the formation of a 2-oxazolidone derivative of the type indicated below:



The following experiments were conducted which established the especially favorable effect of dimethylamine in lowering the cure temperature of Dicy-containing resins.

Two milliliters of liquid dimethylamine (bp 7°C) in a chilled syringe were rapidly introduced and stirred into an intimate mixture of Shell's EPON 828, diglycidyl ether of bisphenol-A (23.13 g) and Dicy (1.48 g). The resulting three-component system contained in a large test tube was placed in an oil bath held at 116°C. Solidification of this system was realized in about 10 minutes whereas, under identical conditions, a resin + dimethylamine mixture required approximately 30 minutes to harden. The EPON 828 + Dicy control showed no signs of solidification with prolonged heating at 116°C. The SP-250 formulation is depicted in Table 1.

1. LaLIBERTE, B. R., and BERGQUIST, P. R. *A Cure Study of Tetraglycidyl Methylene Dianiline Resins with Diuron and Dicyandiamide.* Army Materials and Mechanics Research Center, AMMRC TN 78-5, June 1978.
2. IWAKURA, Y., and IZAWA, S. *Glycidyl Ether Reactions with Urethanes and Ureas in a New Synthetic Method for 2-Oxazolidenes.* J. of Organic Chemistry, v. 29, no. 1, 1964, p. 379-382.
3. LaLIBERTE, B. R. *The Reaction of Diuron with Epoxy Groups.* Army Materials and Mechanics Research Center, AMMRC TN 79-1, January 1979.

Table 1.

Resin (wt %)	Monuron (wt %)	Dicy (wt %)
SP-250 resin (88.6)	3.8	7.5

The 3M system was subjected to an extensive examination; therefore, it was necessary to consider the fact that the SP-250 resin is complex because it is composed of three very distinct epoxides. The weight ratio of these epoxides is shown in Table 2.

Table 2.

Epoxide	Epoxide (wt %)	Dicy (wt %)	Monuron (wt %)
A = ECN 1273 (Ciba Geigy)	45.8	3.88	1.96
B = EPON 828 (Shell)	38.1	3.23	1.63
C = Epoxide 3	4.7	0.40	0.20
	88.6	7.51	3.79

A reasonable amount of Dicy and Monuron was assigned to each of the epoxides and the sum of these materials corresponds with Table 1.

The relationship between the exothermic reaction temperature and the heating rate from a series of DSC runs is expressed[4] below:

$$\log \phi = A/T + B$$

where:

ϕ = heating rate (°C/min) assigned to a sample
T = reaction temperature (°K) of the sample
A = constant, related to activation energy (E_a)
B = constant, related to Arrhenius frequency factor.

The dynamic E_a values reported in this manuscript were calculated by multiplying the slope (A) of the above equation by -2.303R where R is the gas constant.

The dynamic heating curves of the various combination of mixtures in Tables 1 and 2 had sufficient symmetry to prompt the introduction of a type of reaction rate which, to the best of our knowledge, has not been previously reported. The reaction temperature of these mixtures is recorded at the apex of the heating curve and from this point a line drawn perpendicular to the base line seems to bisect the exothermic reaction curve.

A computer program determined the A and B constants of the above DSC equation and upon command, at a given temperature (T), a rate (°C/min) was calculated for

4. CARPENTER, J. F. *Quality Control of Structural Nonmetallic.* Prepared for Naval Systems Command, Washington, DC, Contract N00019-76-C-0138, October 1976.

each mixture. It is speculated that these dynamic scanning rates reflect a rapidity in which a system will approach a 50% cure.

Experiment 1 is the analysis of the SP-250 resin + Dicy/Monuron system. The reaction temperatures of this mixture are shown in the Thermal Analysis Table (Table 3). The Arrhenius plot is shown in Figure 1 and indicated by the designation of the concentration of Monuron which is 3.8% (Table 1). This system has an activation energy (E_a) of 21.84 ± 0.76 kcal/mole. The dynamic scanning rate of the system at 130°C is 2.11°C/min.

Experiments 2 and 3 were conducted to study the effect of decreasing the amount of Monuron in the above system. The concentrations of Monuron are given in Table 3 and the plot of these mixtures (Figure 1) indicates that within 0.9 to 3.8 parts of Monuron the E_a remains constants and the scanning rate significantly decreases as the concentration of the trisubstituted urea becomes smaller.

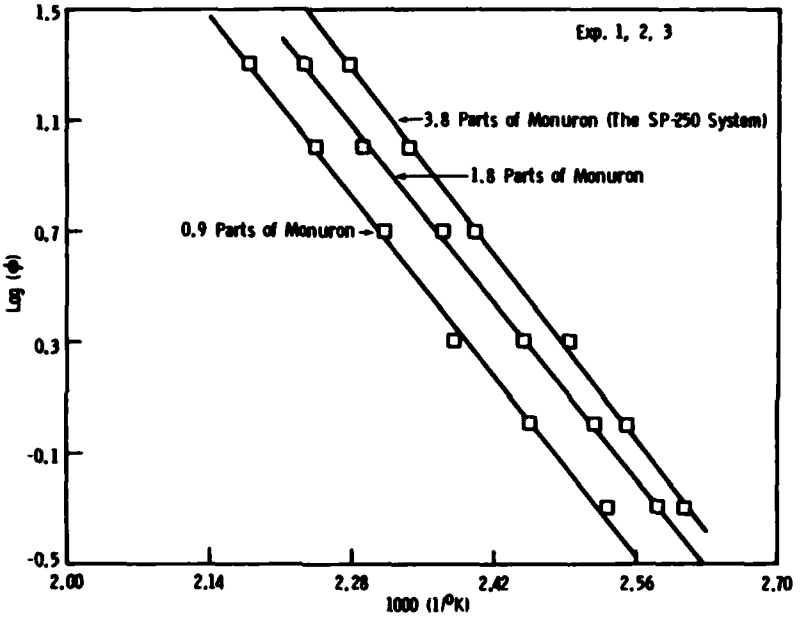


Figure 1.

Experiment 4 represents a modification of 3M's formulation. The Dicy was reduced from 7.5 to 4.0 parts and the amount of Monuron was decreased from 3.8 to 1.8 parts. The modification converts the weight of the reactants from parts per hundred to weight ratio thus 1.8 parts of Monuron indicates a concentration of the urea derivative to be 1.91%. The plot of the thermal data is depicted in Figure 2. The implication of this experiment is that the concentration of Monuron in the SP-250 system is more of an influencing factor on the dynamic scanning rate than the amount of Dicy. Within experimental reliability the data of this mixture is very similar to that of experiment 2.

Experiment 5 is the analysis of the SP-250 resin (88.6) + Monuron (3.8) mixture where the urea concentration is 4.11%. The dynamic E_a was found to be 19.06 ± 0.79 kcal/mole and the scanning rate of this mixture at 130°C was calculated to be 1.64°C/min. The scanning rate of the accelerated SP-250 system was

Table 3. THERMAL ANALYSIS TABLE

Experiment Number	Epoxide (wt)	Monuron (wt)	Dicy (wt)	ϕ (°C/min)	Reaction Temp. (°C)	E_a (kcal/mole)	Scanning Rate (°C/min)
1	SP-250 88.6	3.8	7.5	0.5	110.5	21.84	130°C = 2.11
				1	119	±0.76	120°C = 1.06
				2	128		110°C = 0.51
				5	143.5		
				10	155		
				20	166		
2	SP-250 88.6	1.8	7.5	0.5	114.5	20.83	130°C = 1.45
				1	124	±0.69	120°C = 0.75
				2	135.5		110°C = 0.37
				5	149		
				10	163.5		
				20	175		
3	SP-250 88.6	0.9	7.5	0.5	122	21.18	130°C = 0.78
				1	134.5	±1.18	120°C = 0.40
				2	147		110°C = 0.20
				5	159.5		
				10	172.5		
				20	186		
4	SP-250 88.6	1.8	4	0.5	113	20.01	130°C = 1.55
				1	123	±1.12	120°C = 0.82
				2	135		110°C = 0.42
				5	148		
				10	161		
				20	178		
5	SP-250 88.6	3.8	0	0.5	112	19.06	130°C = 1.64
				1	121	±0.79	120°C = 0.90
				2	132		110°C = 0.47
				5	150		
				10	164		
				20	177		
6,7,8	SP-250 88.6	0	7.5	0.5	172	38.51	200°C = 6.77
				1	178	±2.02	180°C = 1.10
(Results are same with 4 and 2 parts of Dicy)				2	187		160°C = 0.15
				5	197		
				10	204		
9	ECN 1273 45.8	1.96	3.88	0.5	114	21.99	130°C = 1.70
				1	122.5	±1.23	120°C = 0.85
				2	131		110°C = 0.41
				5	145		
				10	158		
				20	171		
10	ECN 1273 45.8	1.96	0	0.5	118	20.33	130°C = 1.18
				1	127	±1.04	120°C = 0.62
				2	138		110°C = 0.31
				5	153		
				10	166		
				20	182.5		
11	ECN 1273 45.8	0	3.88	0.5	172	39.01	200°C = 7.13
				1	178	±1.24	180°C = 1.14
				2	186		160°C = 0.15
				5	196		
				10	204		
12	EPON 828 38.1	1.63	3.23	0.5	103.5	21.80	130°C = 3.96
				1	110	±1.71	120°C = 1.98
				2	118.5		110°C = 0.96
				5	133		
				10	143		
				20	157.5		
13	EPON 828 38.1	1.63	0	0.5	104	17.04	130°C = 2.42
				1	114	±1.37	120°C = 1.41
				2	125.5		110°C = 0.80
				5	141.5		
				10	157		
				20	178		
14	EPON 828 38.1	0	3.23	0.5	166	36.05	200°C = 10.63
				1	172	±0.67	180°C = 1.96
				2	179		160°C = 0.31
				5	192		
				10	199		
15	EPON 828 38.1 ECN 1273 45.8	3.59	7.11	0.5	108	19.11	130°C = 1.96
				1	120	±1.07	120°C = 1.07
				2	131		110°C = 0.56
				5	144		
				10	159		
				20	175		

Table 3 (cont). THERMAL ANALYSIS TABLE

Experiment Number	Epoxide (wt)	Monuron (wt)	Dicy (wt)	ϕ (°C/min)	Reaction Temp. (°C)	E_a (kcal/mole)	Scanning Rate (°C/min)
16	EPON 828 38.1 ECN 1273 45.8	3.59	0	0.5 1 2 5 10 20	111 123 132 151 167 186	17.34 ±1.19	130°C = 1.57 120°C = 0.91 110°C = 0.51
17	EPON 828 38.1 ECN 1273 45.8	0	7.11	0.5 1 2 5 10	170 179 186 195 202	39.66 ±2.93	200°C = 7.83 180°C = 1.22 160°C = 0.16
18	EPON 828 38.1 Epoxide 3 4.7	1.83	3.63	0.5 1 2 5 10 20	109.5 117 125 141 155 169	20.38 ±1.79	130°C = 2.31 120°C = 1.21 110°C = 0.61
19	EPON 828 38.1 Epoxide 3 4.7	1.83	0	0.5 1 2 5 10 20	110.5 124 133 149 165 181	18.44 ±1.05	130°C = 1.59 120°C = 0.89 110°C = 0.48
20	EPON 828 38.1 Epoxide 3 4.7	0	3.63	0.5 1 2 5 10	169 179 185 197 204	36.03 ±2.75	200°C = 6.77 180°C = 1.25 160°C = 0.20
21	ECN 1273 45.8 Epoxide 3 4.7	2.16	4.28	0.5 1 2 5 10 20	115 126 134 149 164 179	20.26 ±1.39	130°C = 1.41 120°C = 0.74 110°C = 0.38
22	ECN 1273 45.8 Epoxide 3 4.7	2.16	0	0.5 1 2 5 10 20	114 128 138 156 171 187	18.13 ±0.67	130°C = 1.23 120°C = 0.69 110°C = 0.38
23	ECN 1273 45.8 Epoxide 3 4.7	0	4.28	0.5 1 2 5 10	173 180.5 188 199 208	36.58 ±0.64	200°C = 5.35 180°C = 0.96 160°C = 0.15
24	Epoxide 3 4.7	0.20	0.40	0.5 1 2 5 10	121 132 141 157 173	20.44 ±1.36	130°C = 0.93 120°C = 0.94 110°C = 0.25
25	Epoxide 3 4.7	0.20	0	0.5 1 2 5 10 20	95 106 118 134 147 164	17.29 ±0.47	130°C = 3.94 120°C = 2.27 110°C = 1.28
	This mixture has two distinct exotherms.			0.5 1 2 5 10 20	123 134 144 162 178 198	18.36 ±1.37	130°C = 0.83 120°C = 0.46 110°C = 0.25
26	Epoxide 3	0	0.40	This mixture is not amenable to thermal analysis.			

Experiment number designates the order in which the data is collected, discussed, and plotted.

Weight (wt) = weight of reactants (see Discussion and Results section).

ϕ = heating rate (°C/min) assigned to cure a sample.

Reaction temperature (°C) of the sample, recorded at the apex of the exotherm.

Scanning rates (°C/min) are calculated at a given temperature and (to the best of our knowledge) this method of evaluating epoxy systems has not been previously reported.

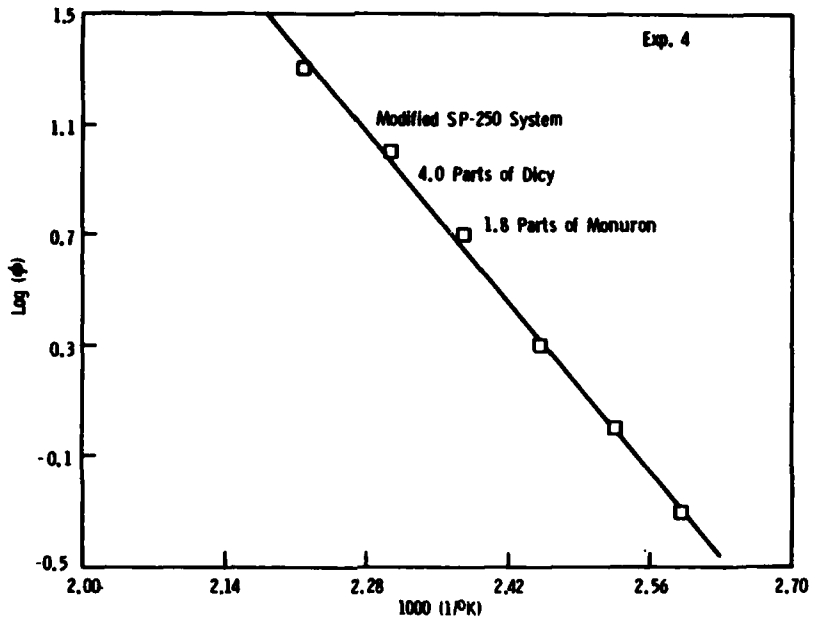


Figure 2.

previously determined to be 2.11°C/min. The difference between the two scanning values is substantial and it was speculated that the Dicy hardening agent enhanced the formation of 2-oxazolidone. Supporting evidence to this speculative view is to be found in a report* which is to be published. The graph of this mixture is designated in Figure 3.

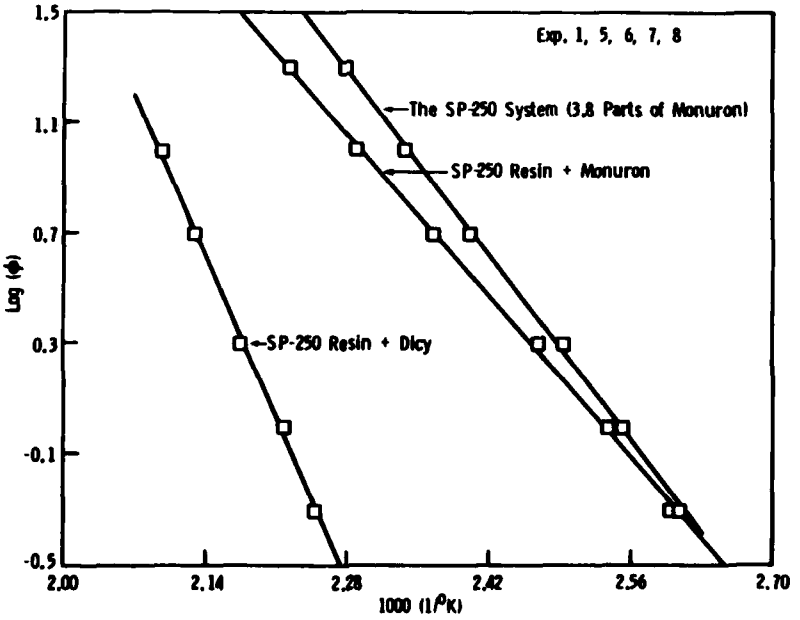


Figure 3.

*SACHER, R. E., and LaLIBERTE, B. R. *Infrared Spectroscopy of the SP-250 Epoxy Resin System.* Army Materials and Mechanics Research Center, AMMRC TR to be published.

Experiments 6, 7, and 8 are the examination of the SP-250 resin (88.6) + Dicy reaction. The resin was mixed with various amounts of the Dicy hardening agent. One mixture observed the formulary integrity of 3M's total formulation (Table 1). Obviously, in the two-component mixture, 7.5 parts of Dicy represent a concentration of 8.5%. The two other mixtures had 2 and 4 parts of the hardening agent. The three mixtures afforded identical data. Consequently, the SP-250 + Dicy plot in Figure 3 represents experiments 6, 7, and 8. The dynamic E_a is 38.51 ± 2.02 kcal/mole and the dynamic DSC scanning rate was calculated to be 6.77°C/min at 200°C.

The above observations prompted further investigation. The mixture with 7.5 parts of Dicy produced a hardened material in 2 hours at 200°C. In contrast, the mixture with 2 parts of Dicy realized a poor cure under identical conditions. The scanning rates did not recognize the difference in the curing chemistry and it would seem, in this case, the values only reflected the element of time to approach 50% reaction. Somewhere, under 2 parts of Dicy, there would most likely be a concentration that would have a substantial effect on the scanning rates.

The three Arrhenius plots in Figure 3 illustrate the synergistic effect of the SP-250 system. The three-component SP-250 + Dicy/Monuron system appears to have a slightly larger dynamic E_a than the SP-250 Monuron reaction. In contrast, the E_a of the resin + Dicy reaction is about two times that of the resin + urea mixture. Thus, the mechanism for the acceleration of Dicy is dependent on a reaction between the resin and Monuron.

Experiments 9, 10, and 11 are the analysis of three ECN 1273 containing mixtures. ECN 1273 is a solid resin which has an epoxy cresol Novolac structure. The mixtures were prepared in compliance with Table 2. The data in Table 3 and Figure 4 indicates the synergy between the hardening agent and the urea derivative.

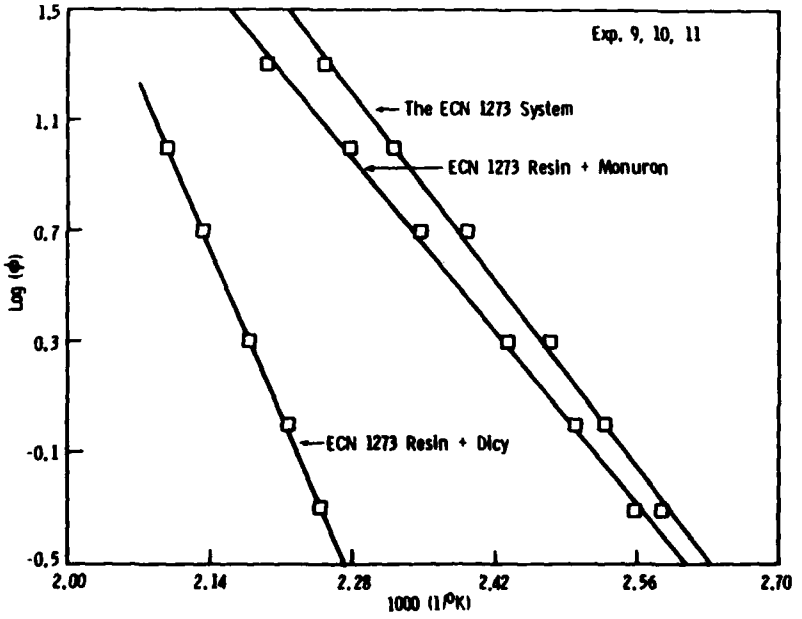


Figure 4.

Experiments 12, 13, and 14 depict the synergistic effect in the EPON 828 mixtures (Figure 5) being rather pronounced.

Experiments 15, 16, and 17 show that the epoxide combination of EPON 828 (38.1)/ ECN 1273 (45.8) afforded mixtures that demonstrated the expected synergistic effect (Figure 6). The scanning rates of these three mixtures, when compared to those of EPON 828 and ECN 1273, appear to be quite reasonable.

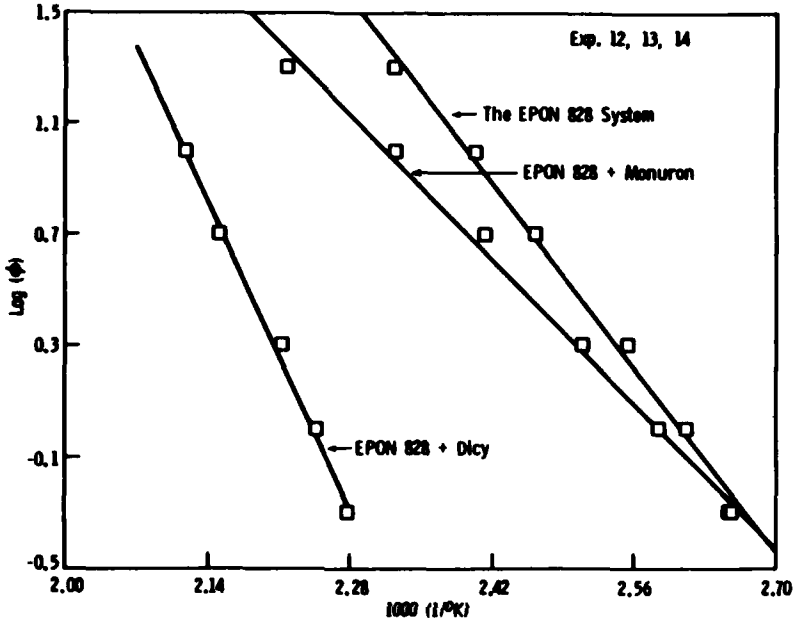


Figure 5.

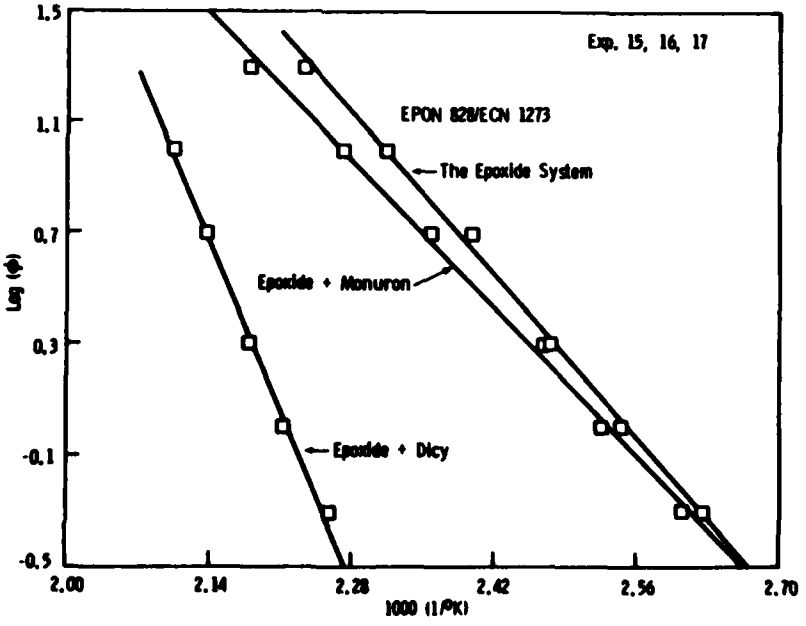


Figure 6.

Experiments 18, 19, and 20: Considering there is only 10.8% of Epoxide 3 in the three-component EPON 828 (38.1)/Epoxide 3 (4.7) + Dicy (3.63)/Monuron (1.83) system, it would be expected that this material would not have a substantial effect on the scanning rates of the EPON 828/Epoxide 3 mixtures. Figure 7 shows the Arrhenius plot of these three mixtures and the three-component system was found to have a scanning value of 2.31°C/min at 130°C. In comparison, the three-component mixture of neat EPON 828 (experiment 12) has a rate of 3.96°C/min. The decrease in the rate seems to be fairly consistent for the two- and three-component systems. A comparison between the rates of experiments 12, 13, 14, 18, 19, and 20 is indicated below:

$$3.96/2.31 \cong 2.42/1.59 \cong 10.63/6.77 \approx 1.52 \text{ to } 1.71.$$

The inference of the above scanning rates is that Epoxide 3 "cools off" EPON 828.

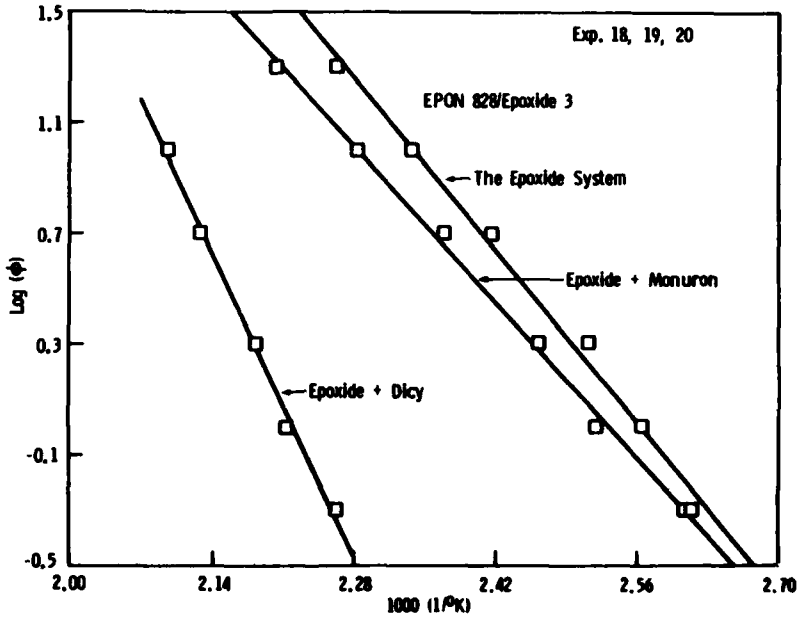


Figure 7.

Experiments 21, 22, and 23 as indicated in Figure 8 is the plot of the ECN 1273 (45.8)/Epoxide 3 (4.7) mixture. Epoxide 3 was subjected to high pressure liquid chromatographic analysis in the laboratory. Epoxide 3 was found to be a mixture and the two main ingredients are monofunctional epoxides.

Experiments 24 and 25: Experiment 25 consists of the Epoxide 3 + Monuron reaction. The heating curve was distinctly bimodal indicating two separate reactions. The E_a's were very similar, however, one reaction had a scanning rate of 3.94°C/min at 130°C which was substantially larger than EPON 828 (2.42°C/min).

The plot of the Epoxide 3 + Dicy/Monuron reaction (Figure 9, experiment 24) appeared to be normal because it converged with one of the epoxide + Monuron graphs. The position of this plot seemed to favor one of the Epoxide 3 + Monuron reactions. Therefore, we conducted an isothermal DSC analysis of the two-component mixture

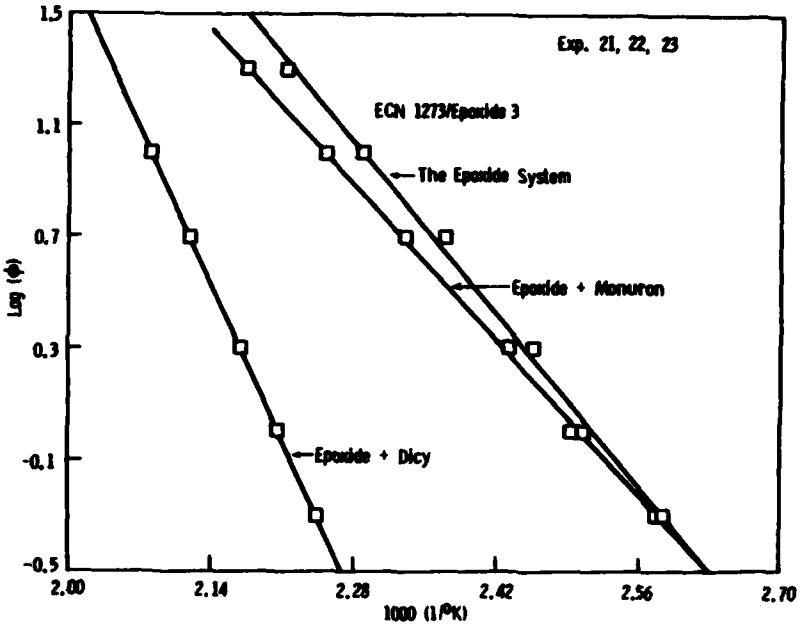


Figure 8.

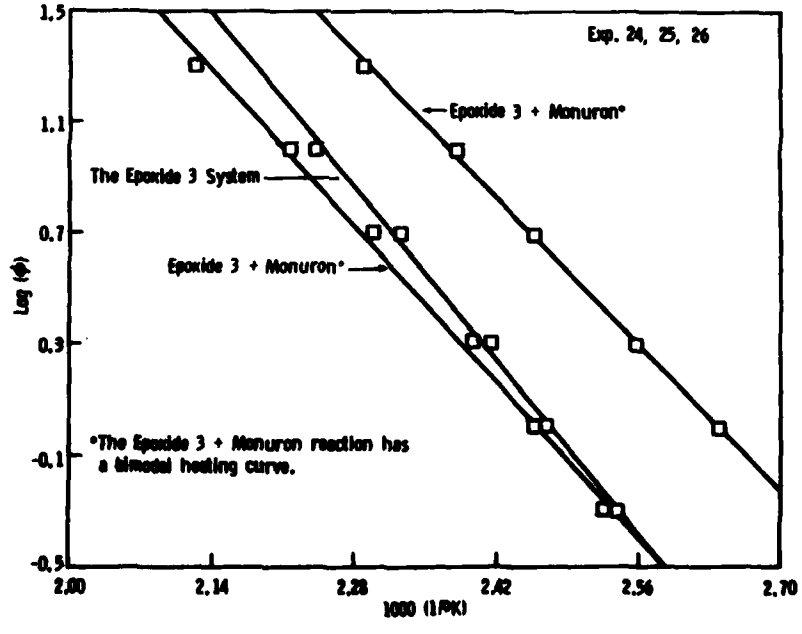


Figure 9.

that resulted in an appreciable weight loss which suggested some decomposition. The dynamic analysis of the Epoxide 3 + Dicy mixture (experiment 26) inferred extreme decomposition. Thus, in the reaction of the three-component system, it is conceivable that there may have been some selective decomposition.

The role of Epoxide 3 in the SP-250 system appeared to be complex. Further investigation is required for the SP-250 system. Additional information regarding the DSC dynamic scanning rates will be forthcoming.

Some heats of reaction were measured. The normalized area of the exotherm of the EPON 828 (38.1) + Monuron (1.63) reaction became progressively smaller as the heating rate was increased when experimentation was conducted in open aluminum pans. These values were reproducible. Failure to achieve a constant area may be attributed to the rapidity with which dimethylamine escapes from its environment. Further investigation indicated that an analysis conducted at an especially slow heating rate of 0.5°C/min afforded results that were in agreement with areas recorded isothermally. Thus, the calculation of the extent of reaction did not present a serious problem. Monuron underwent considerable reaction with EPON 828 at 90°C in 2.5 hours.

With the increase of the concentration of Monuron in a pure resin the heat of reaction was constant regardless of the heating rate (0.5°C/min to 10°C/min). It appeared that the abundance of dimethylamine favored the completion of the resin + amine reaction.

EXPERIMENTAL

DSC measurements were conducted in open aluminum pans with a DuPont 990 thermal analyzer fitted to a 920 DSC module under static air. Reaction temperatures were recorded at the apex of the heating curve.

PREPARATION OF MIXTURES

For this study the SP-250 resin was prepared. The weight ratio of the epoxides is given in Table 2. These three epoxy materials were blended together at 92°C and the resulting mixture is extremely viscous at ambient temperatures. Mixtures were prepared with approximately 5 grams of epoxide(s). Weightings were carried out to three significant places and the mixing procedure varied according to the physical state of the reactants. Blends of solid materials such as ECN 1273, Dicy, and Monuron were prepared with a mortar and pestle.

The liquid epoxides, such as EPON 828 and Epoxide 3, were mixed with Monuron in small beakers at ambient temperatures with a spatula. The low viscosity of Epoxide 3, with the limited solubility of Monuron, particularly Dicy, was such that the precipitation of these materials caused some difficulty in sampling.

The viscosity of the SP-250 resin prevented mixing at ambient temperatures. The resin was heated in a 90°C oven. With a marked increase in flow, and upon removal of the resin from the heating source, Dicy was blended into the resin. This procedure was repeated several times to ensure proper mixing. The oven

temperature was reset for the preparation of Monuron mixtures because the urea derivative reacted with the epoxides at a lower temperature than the hardening agent.

The resin combinations of Epoxide 3 and ECN 1273 were prepared as follows: Epoxide 3 dissolved in methylene dichloride was added to the solid blend of ECN 1273/Monuron and prolong stirring resulted in a past-like material. The residual solvent was not removed to facilitate sampling.

The activation energies were calculated using a Hewlett Packard 980 computer.

CONCLUSIONS

The dynamic E_a of the SP-250 + Dicy mixture was found to be 38.51 ± 2.02 kcal/mole. In contrast, the three-component SP-250 resin + Dicy/Monuron system underwent reaction with greater facility because the activation energy indeed decreased considerably. The value was calculated to be 21.84 ± 0.76 kcal/mole. Significantly, this value is not much different from the resin + Monuron mixture which is associated with an E_a of only 19.06 ± 0.79 kcal/mole. Consequently, the lowering of the cure temperature of Dicy-containing epoxy resins may be explained via a reaction between Monuron and the resin and in this process the reactivity of Dicy is dramatically enhanced.

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Bernard R. LaLiberte and Robert E. Sacher

Technical Report AMMRC TR 83-17, April 1983, 10 pp -
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The synergistic effect of dicyandiamide and Monuron which takes place in the hardening of epoxy resins was investigated by differential scanning calorimetric analysis conducted under dynamic conditions. The cure behavior was illustrated by the examination of three distinct systems: SP-250 epoxy resin + dicyandiamide (Dicy), resin + Dicy/Monuron, and resin + Monuron. The activation energies of these systems were found to be 39, 22, and 19 kcal/mole, respectively. The by-product of the resin + Monuron reaction is dimethylamine and it was found that this amine is able to enchance the reactivity of dicyandiamide dramatically. Mixtures pertinent to the SP-250 formulation were examined and the interpretation of the thermal data afforded certain speculations.

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